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ELECTROLYTIC SEPARATION OF AL3NI FIBERS FROM THE EUTECTIC ALLOY—ETC(U)

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oxidized within the potential range of -0.8 to +0.5 volt (vs. S.C.E.) in a 1M potassium hydroxide electrolyte. This decreased rate of oxidation of aluminum in the Al₃Ni fibers is correlated with the low rate of diffusion of the aluminum in the Al₃Ni orthorhombic crystals.

The procedure does not require the stringent conditions as in other methods of producing Al₃Ni fibers from eutectic alloys. The method has the additional advantage of being applicable to a continuous process where the fibers can be removed and the electrolyte replenished.

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Electrolytic Separation of Al₃Ni Fibers From the Eutectic Alloy, Al-Al₃Ni

1. INTRODUCTION

Unidirectional solidification of eutectic alloys have received considerable attention during the last decade.^{1, 2} The microstructures of these eutectic alloys have also been reviewed,³ and have been classified as normal and abnormal. The normal microstructures are mainly the lamellar or fibrous type that are formed by the simultaneous growth of the two solid phases. The abnormal microstructure is formed when unequal linear growth of the two solid phases occurs. Many recent studies have been undertaken to determine and evaluate the potential use of directional solidified composite eutectics in the area of device applications. The eutectics of the normal type with the ordered structure appear to lend themselves extremely well to devices. The possible use of the separated fibers from the unidirectional solidified eutectics in various applications has also been sought.

(Received for publication 12 December 1979)

1. Bibliography on Fibers and Composite Materials, 1972-1978. Compiled by D. M. Johnson, Metals and Ceramics Information Center, Battelle's Columbus Laboratories, Columbus, Ohio.
2. Bibliography on Fibers and Composite Materials, 1969-1972. Compiled by J. N. Fleck. Metals and Ceramic Information Center, Battelle's Columbus Laboratories, Columbus, Ohio.
3. Hogan, L. M., Kraft, R. W., and Lemkey, F. D. (1971) Advances in Materials Research, Eutectic Grains 5:83-126.

This paper describes an electrolytic process in which fibers are separated from the matrix in excellent condition.

Various uses of the unidirectional solidified eutectic alloys have been pursued in the areas of electronics, magnetics, and optical devices. In 1963, Liebmann and Miller⁴ reported the thermoelectric properties of the InSb-Sb eutectic. Similar studies with the Bi₂Te₃-Te eutectic were reported by Galasso.⁵ Improvement of coercive forces of magnetic materials by the unidirectional solidification of eutectic alloys have been reported by Glardon and Kurz.⁶ Lithium ferrite-lithium niobate and lithium ferrite-lithium tantalate were directionally solidified to form eutectic alloys containing a ferromagnetic and a piezoelectric phase.⁷ Directional eutectic alloys have been reported to polarize infrared radiation.⁸ The use of aligned alloys as superconductors to avoid the limitations of brittle conductors is under active investigation.^{9, 10, 11} Recent studies^{12, 13} have shown that the application of these superconductors is now a reality in the areas of power transmission and high-field magnets. The Al-Al₃Ni eutectic has been proposed as a low-temperature power transmission cable material.¹⁴ Many eutectics have shown promise as materials for cold cathodes.^{15, 16} The high density electron emitter, LaB₆, has been successfully prepared as an aligned eutectic with rods of LaB₆.¹⁷ The possibility of producing solar cells of SnSe-SnSe₂ with the alternating layers of p- and n-materials has been undertaken.¹⁸ Aligned eutectics may also have many potential applications in the energy technologies. These alloys may find applications as catalysts in electrochemical devices as well as electrodes in photoelectrolysis systems.

These composites offer the opportunity of combining the desirable properties of two different phases to produce a device which is superior to that of the best single phase material. Aligned eutectics may exhibit completely new properties not found in the separate phases. Newham, Skinner and Cross¹⁹ have discussed the design of unidirectional solidified eutectics for use as piezoelectric transducers or as pyroelectric detectors. Van Suchtelen²⁰ has introduced the concept of product properties.

Many potential applications exist for the use of the separated fibers from the unidirectional solidified eutectics. This laboratory has been particularly interested in the use of these fibers in military applications. The separated metallic fibers from the eutectics may have improved characteristics as chaff in establishing communication of limited duration between nonadjacent troposcatter stations.²¹ These separated fibers may also prove beneficial as ECM obfuscating agents.²² Metallic fibers may also exhibit desired characteristics for use in variable permittivity liquid phase shifters.²³ The present materials that are being investigated

Because of the large number of references cited above, they will not be listed here. See References, page 21.

in phase shifters tend to "paint" or coat the interior of the wave guide. These electronically controlled phase shifters are currently needed in existing air traffic control systems and in planned airport surveillance radar. Other non-military uses are found in the area of fuel storage (primarily metal hydrides) where the high surface area of fibers offer an excellent storage capacity for hydrogen. These eutectics fibers may also exhibit capabilities as catalysts where high surface areas are available.²⁴ The Al₃Ni fibers may possibly be used as starting materials in the production of the Raney nickel catalyst.²⁵ The possibility of dispersing the eutectic fibers in an insulating medium may show promise as an efficient photo-thermal converter of solar energy. Granqvist and Hundre²⁶ have analyzed the roles of the medium thickness, substrate metal, particle shape and orientation, possible dielectric cores in the particles, dielectric permeability of the embedding medium and of graded volume fractions of metal in solar converters.

In order to evaluate the many potential applications of the separated fibers, methods have to be developed to separate the fibers without damage in good yield and at low cost. Subsequently, these methods may be required to produce the product on a unit-operation level. A study at this laboratory was undertaken to separate the Al₃Ni fibers from the eutectic alloy, Al-Al₃Ni. These fibers are of interest as materials for chaff and for use in phase shifters.

Hertzberg, Lemkey, and Ford²⁷ used an acid leaching to separate the Al₃Ni fibers from the Al matrix and found that the fibers had to be removed from the acid solution as rapidly as possible and thoroughly washed in water to minimize the possibility of surface attack. Hussey, et al²⁸ described an electrolytic procedure to remove the Al₃Ni fibers using two molten salts as the electrolyte. These molten salts require inert atmospheres and high temperatures. This paper reports a method where high quality Al₃Ni fibers are obtained using 1M potassium hydroxide as the electrolyte. The results show that the Al₃Ni fibers are not attacked by the hydroxide solution in the present procedure. The advantages of the present method

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24. Lemkey, F.D., Golden, G. and Brooks, C.S. (1976) Fibrous eutectic alloy catalysts. Abstracts, annual meeting, Material Research Society. Nov. 15-17, Cambridge, Mass.
 25. Remy, H. (1956) Treatise on Inorganic Chemistry, Vol. II, p. 716, Elsevier Publishing Company, New York.
 26. Granqvist, C.G. and Hundre, O. (1979) Selective absorption of solar energy in ultrafine metal particles; model calculations, J. Appl. Phys. 50:1058-10.
 27. Hertzberg, R.W., Lemkey, F.D. and Ford, J.A. (1965) Mechanical behavior of Lamellar (Al-CuAl₂) and whisker type (Al-Al₃Ni) unidirectionally solidified eutectic alloys, Trans. Met. Soc. AIME 233:342-354.
 28. Hussey, C.L., Nardi, J.C., King, L.A. and Erbacher, J.K. (1977) Electrolytic etching of aluminum from an Al-Al₃Ni two-phase matrix in chloride containing molten salts, J. Electrochem. Soc. 124:1451-1454.

over the other two are obvious. The process has the additional advantage of being applicable to a continuous process where the fibers can be removed and the potassium hydroxide replenished.

2. EXPERIMENT

The eutectic alloy, Al-Al₃Ni, used in the present study was prepared from 3N7-nickel and 5N-aluminum.* A master alloy slug containing the eutectic composition of aluminum-nickel (5.7 wt. % Ni) was prepared in an alumina crucible under argon. The thoroughly mixed alloy was then used for the production of the unidirectional solidified Al-Al₃Ni alloy. Unidirectional solidification of the alloy was carried out using a Bridgeman arrangement with a platinum wound, electric resistance furnace with a direct water-cooled chill. Solidification was carried out in graphite crucibles under argon with a soak temperature of 750°C (eutectic temperature, 640°C). Typical pull rates were 4.2, 5.0 and 8.1 cm/hr. The aluminum-nickel alloys of various compositions were prepared in alumina crucibles. The mixtures were heated to 1700°C in a Centorr High Temperature Furnace with tungsten mesh heaters under argon. The mixtures were allowed to remain at this temperature for approximately one-half hour to insure complete mixing. The highest melting point of the various compositions of aluminum and nickel mixtures (50 Atom %) is 1638°C.²⁹ The NiAl alloys were rapidly cooled by removal of the heat.

The electrochemical measurements were carried out with the apparatus and cell shown in Figures 1 and 2. The anodic polarization curves were determined by varying the output potential of the Model 173 Potentiostat (Princeton Applied Research, PAR) with the Model 17 Programmer (PAR). The current was monitored with a Model 176 Current-to-Voltage Converter (PAR) and recorded with a Sargent MR Recorder. The scan rate was maintained at 50 mv/sec throughout the study. All electrochemical measurements were carried out at room temperature.

The cell used in the study is shown in Figure 2. The reference electrode was a saturated calomel electrode. The anodic polarization curves for aluminum were obtained with an aluminum wire (1 mm, diameter) as the working electrode. The counter electrode used throughout the study was platinum with dimensions of 2.0 × 2.3 × 0.02 cm.

*Supplied by Alfa Products, Ventron Corp., Danvers, Mass.

29. Alexander, W.Q. and Vaughan, N.B. (1937) The constitution of the nickel-aluminum system, J. Inst. Metals 61:247-263.

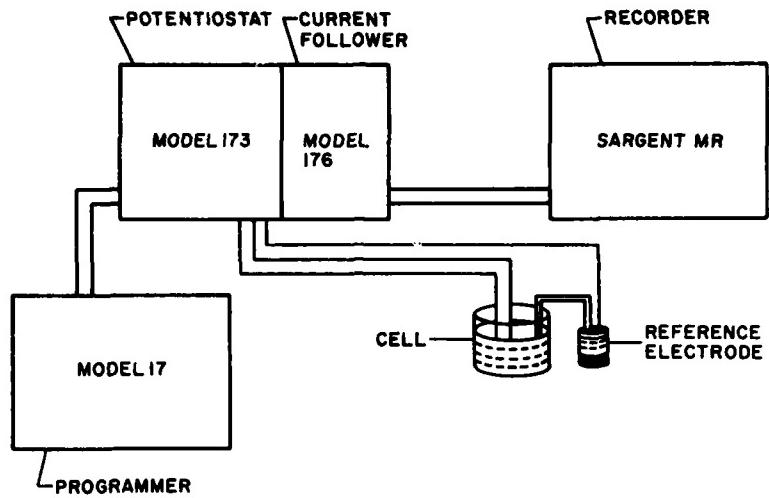


Figure 1. Schematic Representation of Apparatus Used for the Study of the Anodic Dissolution of Aluminum Matrix from Al_3Ni Fibers

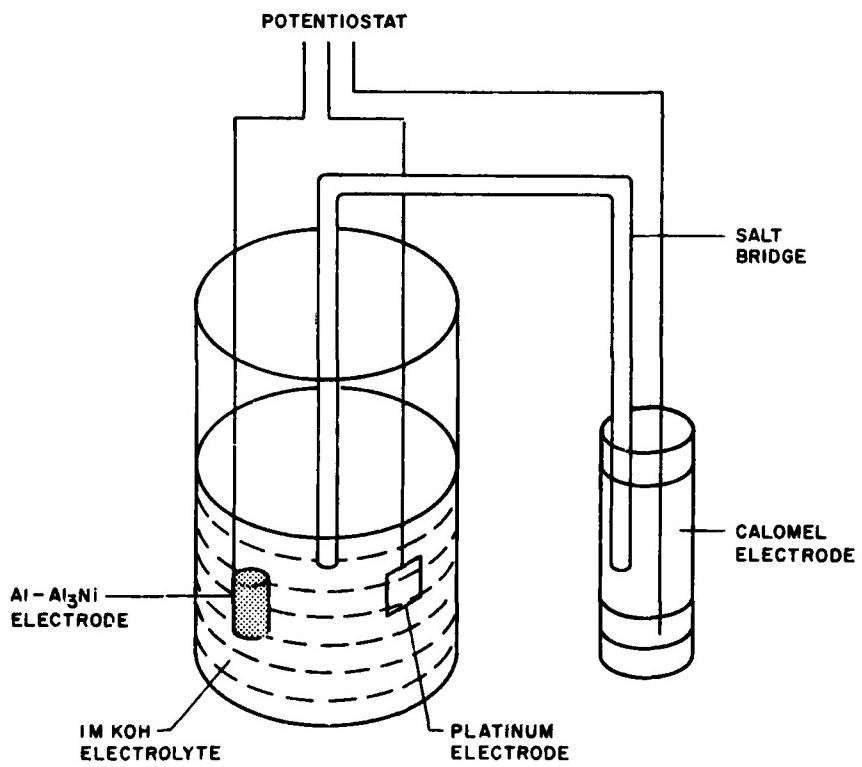


Figure 2. Electrochemical Cell Used in the Anodic Dissolution Studies. Reference electrode, saturated calomel electrode

Anodic polarization studies of the Al-Al₃Ni alloy were performed using an ingot of the alloy as the working electrode. Contact was made to the ingot by encircling the alloy with a platinum wire. Anodic polarization measurements of the aluminum-nickel alloys were performed using the same procedure. The electrolyte used in all the studies was a 1M solution of potassium hydroxide.

The electrochemical oxidation of the separated Al₃Ni fibers was studied with the fabricated electrode shown in Figure 3. The Al₃Ni fibers prepared by the present method were separated, washed with water and air dried. The Al₃Ni fibers were contacted to the platinum wire by means of silver paste. The tip of the platinum electrode was immersed in the silver paste* and, with a thin film of paste on the electrode surface, rolled in the dried Al₃Ni fibers. The electrode was operational since typical anodic polarization curves were obtained for aluminum when small particles of aluminum were substituted for the Al₃Ni fibers.

Energy dispersive X-ray analyses of the Al₃Ni fibers were performed with an EDAX Model of 707B X-ray Spectrometer.

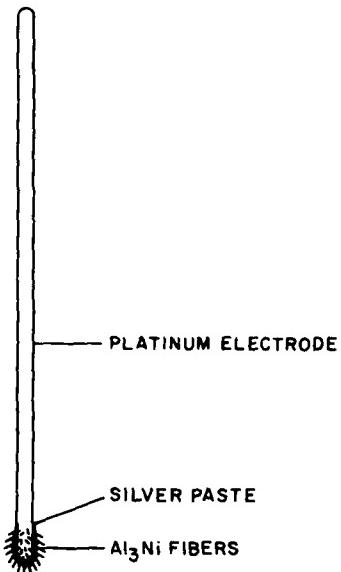


Figure 3. Electrode Constructed to Measure Potentiostatic Anodic Polarization of the Al₃Ni Fibers

3. RESULTS

Unidirectional solidification of the master alloys containing 5.7 percent nickel with aluminum produced ingots with aluminum matrix containing Al₃Ni fibers. A reproduction of the microstructure of the Al-Al₃Ni eutectic is shown in Figure 4. The length of the fibers has a median value of approximately 180 μm with a diameter of 5 μm . Changes in morphology are observed with changes in growth rate. Lemkey, Hertzberg, and Ford³⁰ have studied the microstructure and crystallography

*The silver paste was the SPI-5060 product of SPI Supplies Div., Structure Probe, Inc., West Chester, Pa. The paste was composed of 70 percent solids.

30. Lemkey, F. D., Hertzberg, R. W. and Ford, J. A. (1965) The microstructure, crystallography, and mechanical behavior of unidirectionally solidified Al-Al₃Ni eutectic, *Trans. Met. Soc. AIME* 233:334-341.

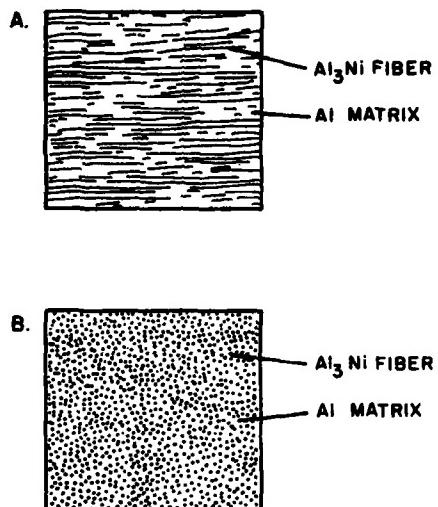


Figure 4. Microstructure of Al-Al₃Ni Eutectic Alloy Prepared by Unidirectional Solidification.²⁷ A. Longitudinal section (mag. 160X). B. Transverse section (mag. 400X)

of the Al-Al₃Ni alloys. The microstructures of the NiAl alloys with the various compositions were not studied.

The aluminum wire and the ingots of the Al-Al₃Ni eutectics were used directly in the electrochemical studies. The NiAl alloys were polished with 600 grit SiC. The electrochemical results were of the same order of magnitude for the polished and unpolished NiAl alloy specimens.

The anodic polarization of aluminum in 1M potassium hydroxide electrolyte produces the aluminate ion, H₂AlO₃⁻, according to the following equation



In alkaline solution the oxide film on the surface of the metal is eliminated with the subsequent oxidation of the aluminum. The potential of the half-cell reaction is +2.35V (vs. H₂/H⁺ electrode).³¹ The oxidation of aluminum should extend from the potentials where the reduction of the hydroxide system is occurring to the potential area overlapping the oxidation of the hydroxide ion. The anodic and

31. Latimer, W.M. and Hildebrand, J.H. (1940) Reference Book of Inorganic Chemistry, p. 477, Macmillan Company, New York.

cathodic polarization of the 1M potassium hydroxide system at a platinum wire electrode is shown in Figure 5. Below values of -1.02 volts (vs. S. C. E.), the reduction of water with the liberation of hydrogen is indicated by the increase in positive current with decreasing potentials. At values greater than +0.57V (vs. S. C. E.), oxidation of the hydroxide ion takes place. Between these values (-1.02V to +0.57V) the hydroxide system is electrically stable. The potential range found for nickel electrodes was from -1.3V to +0.57V (vs. S. C. E.). These results indicate that aluminum can be oxidized in the potential interval of approximately -1.0V to +0.5V (vs. S. C. E.) without any apparent complications.

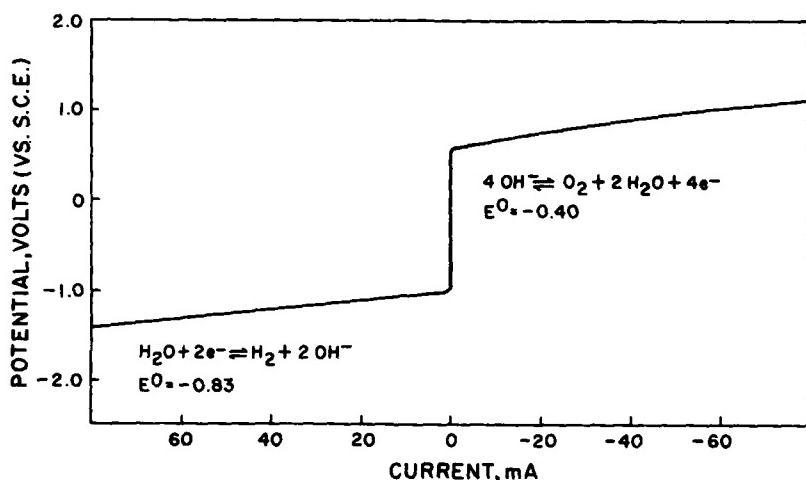


Figure 5. Potentiostatic Anodic and Cathodic Polarization of Platinum Electrode in 1M Potassium Hydroxide Electrolyte (Room Temperature)

Figure 6 illustrates the anodic oxidation of three samples of aluminum having different surface areas. These samples were run in order to gain insight into the potential range of aluminum oxidation and its characteristics. The initial increase of the negative current representing the oxidation of aluminum is observed to begin at a potential value of -1.78V (vs. S. C. E.). The positive current (not shown) at potentials between -1.78V (vs. S. C. E.) and the initial potential for Al oxidation represents the offsetting currents between the reduction of the hydroxide system and the oxidation of aluminum with the reduction being dominant.³² Oxidation of the

32. Pourbaix, M. (1974) Atlas of Electrochemical Equilibria in Aqueous Solutions, p. 171, National Association of Corrosion Engineers, Houston.

hydroxide ion does not accompany the oxidation of the aluminum in the potential range greater than +0.5V (vs. S.C.E.). This is evident by the lack of oxygen evolution and the slow rate of change of the negative current. The convex area of the curve for the anodic polarization of the aluminum having a surface area of 2.5 cm^2 is reproducible and its origin has not been investigated. Current densities for the three samples are found to be directly proportional to the surface areas of the aluminum above the potential of -0.5V (vs. S.C.E.). Kamel, Awad, and Kassab³³ have recently studied the anodic dissolution of aluminum in sodium hydroxide solutions.

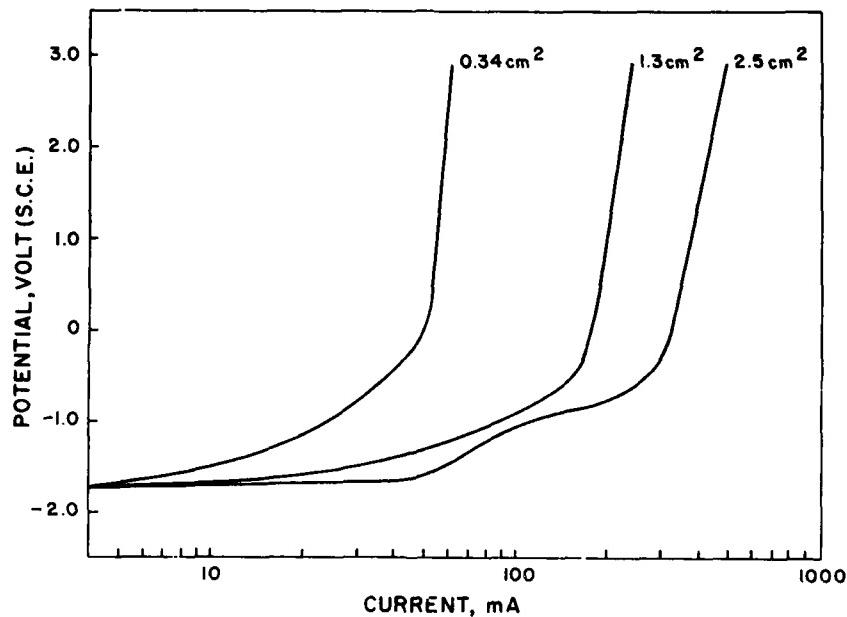


Figure 6. Potentiostatic Anodic Polarization Curves for Three Aluminum Samples. Surface areas of samples, 0.32, 1.3 and 2.5 cm^2 (electrolyte, 1M KOH; Room Temperature)

The anodic polarization of three samples of the Al-Al₃Ni eutectic is shown in Figure 7. The oxidation of the aluminum in the eutectic is observed to begin at a higher potential (-1.34V (vs. S.C.E.)) than that of aluminum (-1.78V (vs. S.C.E.)). This difference in potential is probably related to the smaller concentration of the aluminum being oxidized in the eutectics. Maximum anodic dissolution of the

33. Kamel, K. H. M., Awad, S. A. and Kassab, A. (1979) Mechanism of electrochemical reactions at aluminum electrodes in NaOH solutions, *J. Electroanal. Chem.*, 99:121-125.

aluminum matrix occurs in the potential range of -0.8V to +0.5V (vs. S.C.E.). Each curve shows a small decrease in current after a potential of approximately -0.43V (vs. S.C.E.) has been reached. This small decrease could possibly be due to the aluminum undergoing a slight amount of passivation in the presence of the Al_3Ni fibers. At the potential of +0.75V (vs. S.C.E.) an increase of the positive current is observed which is due to the evolution of oxygen.

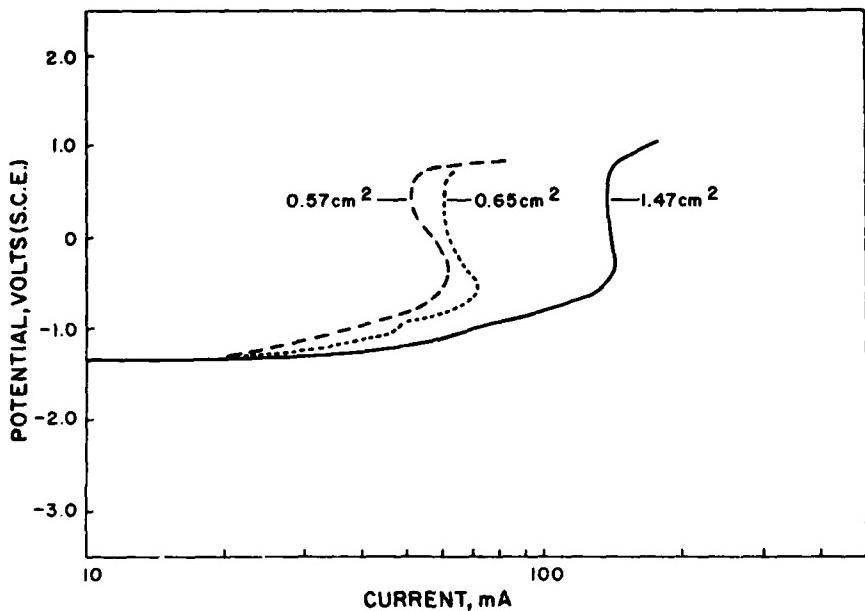


Figure 7. Potentiostatic Anodic Polarization Curves for Three Samples of the Al- Al_3Ni Alloy. Surface areas of alloy samples, 0.57, 0.65 and 1.47 cm^2 (electrolyte, 1M KOH; room temperature)

The current vs. time relationship for the dissolution of aluminum from the Al- Al_3Ni eutectic is shown in Figure 8. The initial reaction of the dissolution of the aluminum is the elimination of the oxide film as represented by the following reaction



This process is followed by the dissolution of aluminum as shown in Eq. (1). Subsequent experiments will show that only the aluminum present in the Al matrix is being oxidized. The aluminum present in the Al_3Ni fibers remains inactive in the anodic oxidation of the alloy. Figure 8 shows that the current decreases with time.

This decrease in current is attributed to the decreased availability of the aluminum in the matrix and possibly to its transport properties.

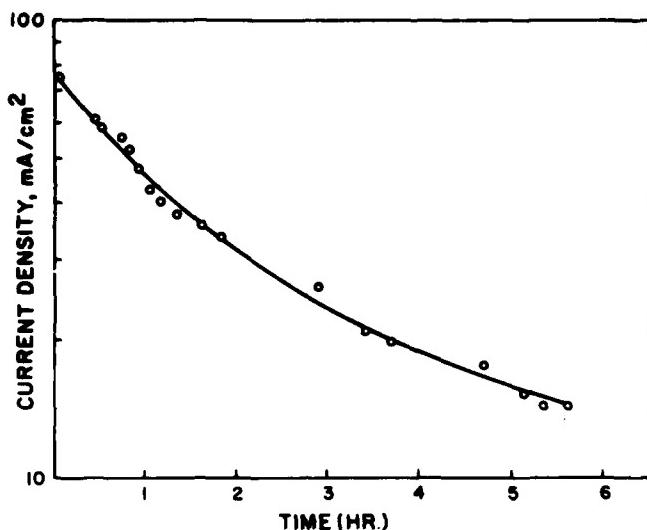


Figure 8. Variation of Current Density with Time Accompanying the Anodic Dissolution of the Al Matrix from the Eutectic Alloy, Al-Al₃Ni. Potential, -0.3V (vs. S.C.E.); sample area, 1.04 cm² (electrolyte, 1M KOH; room temperature)

Figure 9 is the electron photomicrograph of the Al₃Ni fibers produced from the electrolysis of the Al-Al₃Ni eutectic alloy at -0.4V (vs. S.C.E.) for 45 minutes. Similar results were obtained at potentials of -0.2V and -0.3V (vs. S.C.E.). The photomicrograph illustrates the excellent condition of the Al₃Ni fibers that are separated from the Al matrix. Energy dispersive X-ray analysis verified the composition of the fibers to be Al₃Ni. These results also indicated that the aluminum in the fibers remains intact during the anodic polarization of the aluminum matrix.

The above results indicate that the aluminum in the Al₃Ni fibers is not being oxidized or at an immeasurable slow rate in the anodic polarization studies of the Al-Al₃Ni eutectic alloy. This was further substantiated when only a limited attack occurred to the Al₃Ni fibers when exposed to 1M potassium hydroxide solution overnight. In order to substantiate whether the aluminum in the Al₃Ni fibers is undergoing oxidation, electrochemical studies were carried out with the Al₃Ni fibers.

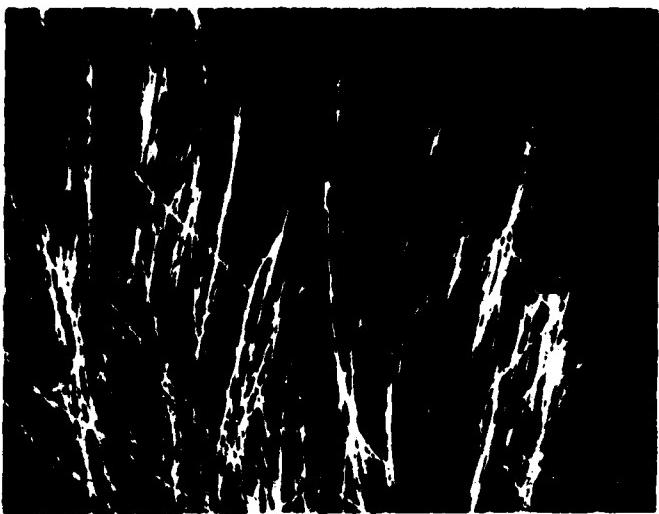


Figure 9. Microstructure of the Al₃Ni Fibers Separated by the Anodic Dissolution of the Al Matrix from the Eutectic Alloy, Al-Al₃Ni (mag. 500X)

Anodic polarization studies were performed with the separated Al₃Ni fibers using the specially fabricated electrode shown in Figure 3. The results of the anodic polarization of the fibers using this electrode is exhibited in Figure 10. There are no differences observed between the anodic current for the electrode with only the silver paste and for that with the silver paste plus the Al₃Ni fibers. The electrode is functional since typical aluminum anodic polarization curves are obtained when the fibers are replaced with small particles of aluminum. Although the surface area of the Al₃Ni fibers is unknown, an amount sufficient to produce a measurable current was observed to be present. These results suggest that the aluminum in the fibers is protected from oxidation by either the presence of nickel or by some other mechanism.

A series of experiments were performed to observe the effect of nickel on the anodic polarization of aluminum in aluminum-nickel alloys. A number of alloys were prepared with increasing concentrations of nickel extending from 0 at.% to 50 at.% Ni. The results obtained from the anodic polarization studies with these alloys are presented in Figure 11. The current densities of the various polished alloys obtained at -0.5V (vs. S.C.E.) are presented as a function of the nickel concentration. The current densities reported for the Al and the 50 atom % alloy are the unpolished values. The curve shows that increasing the nickel concentration decreases the rate of oxidation of the aluminum in these alloys.

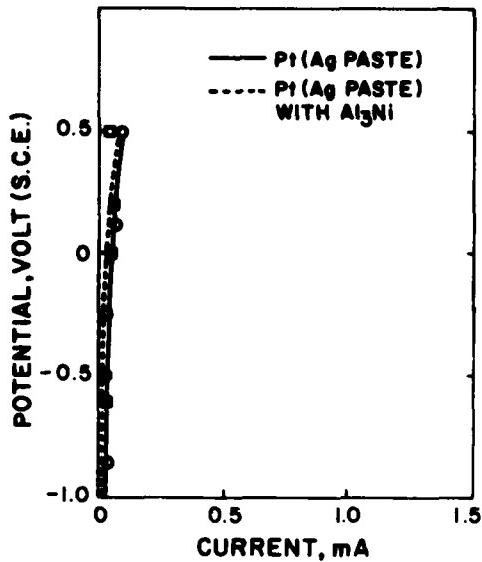


Figure 10. Currents Accompanying the Anodic Polarization of the Platinum (Ag paste) Electrode With and Without Al₃Ni Fibers (electrolyte, 1M KOH; room temperature)

Hutchings and Lorette³⁴ showed in their study of the oxidation kinetics of NiAl alloys at 1173°K that the oxidation rate decreased in a similar fashion with a minimum at about 58 at.% Ni. They related this decrease in oxidation rate to the activity of the aluminum at the metal/oxide interface. The lower the activity or diffusion of the aluminum in the alloy, the lower the rate of oxidation of the aluminum. This relationship of activity to oxidation rate of an alloy is based on the theoretical analysis of diffusion processes by Wagner.³⁵ Comparison of the current observed with the stoichiometric equivalent of 3 Al to 1 Ni in the alloy to that of the Al₃Ni fibers indicate that the aluminum environment is distinctly different in the fibers. A current density of 25 mA/cm² was obtained with the 3Al:Ni alloy while no measurable current was observed with the Al₃Ni fibers.

34. Hutchings, R. and Lorette, M. H. (1978) Compositional dependence of oxidation rates of NiAl and CoAl, *Met. Sci.* 12:503-510.

35. Wagner, C. (1952) Theoretical analysis of the diffusion processes determining the oxidation rate of alloys, *J. Electrochem. Soc.* 99:369-380.

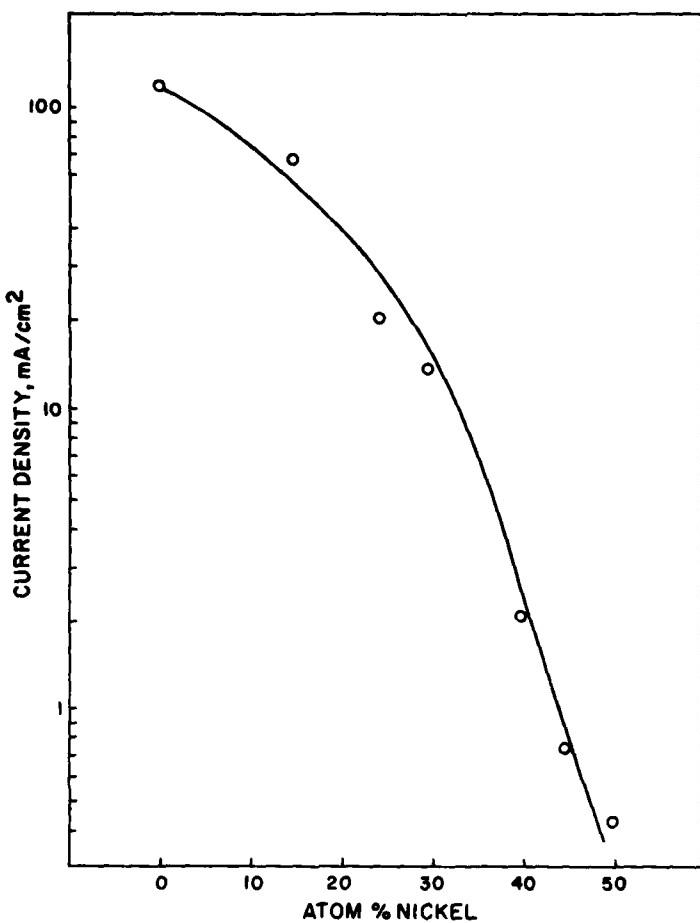


Figure 11. Effect of Nickel Concentration on the Current Densities Accompanying the Potentiostatic Anodic Polarization of Aluminum in Various Aluminum-Nickel Alloys (potential, -0.5V (vs. S.C.E.); electrolyte, 1M KOH; room temperature)

4. DISCUSSION

This paper demonstrates that Al_3Ni fibers can be removed from the eutectic alloy, $\text{Al}-\text{Al}_3\text{Ni}$, by an electrolytic method. The fibers are obtained in excellent condition since the aluminum in the fibers has remained intact during the electrolytic oxidation of the aluminum matrix. The results show that the aluminum in the fibers is protected from oxidation. Similar results of this protection of aluminum in NiAl alloys have been attributed to the presence of nickel by other researchers.³⁴ Mechanisms to explain this decrease in oxidation in the presence of nickel have

also been described by Jost.³⁶ These authors have related the decrease of the oxidation of metals in alloys to their decreased activities (diffusion) at the metal/oxide interface. The rate of diffusion is a function of the bulk activity of the reactive metal according to Fick's diffusion laws. Comparison of the results of the oxidation of aluminum in the stoichiometric alloy (3Al:Ni) to that of Al in the Al₃Ni fibers indicates that the structural properties of the fiber plays an important role in the decreased rate of oxidation of aluminum.

Diffusion of metal atoms and ions require low energies of activation in grain boundaries.^{37, 38} The diffusion of aluminum in the aluminum-nickel alloys is probably relatively high since these solids consist mostly of grain boundaries. The Al₃Ni fibers have an orthorhombic structure³⁹ and contain relatively few grain boundaries. Therefore the diffusion of aluminum in the Al₃Ni fibers would require large energies of activation for diffusion and would be at a minimum. The results of the present study show that the rate of oxidation of the aluminum in the alloys and fibers is probably governed by the diffusion process of aluminum in each. A high rate of oxidation is observed with the aluminum-nickel alloy while little or no oxidation of aluminum occurs in the orthorhombic fibers.

The difference in diffusion of aluminum in the Al matrix and the Al₃Ni fibers makes it possible to separate the fibers from the matrix electrolytically. The same mechanism can also explain the results obtained by Hussey, King, and Erbacher.²⁸

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